28 March 1997

ELSEVIER

Chemical Physics Letters 267 (1997) 460–466

CHEMICAL PHYSICS LETTERS

Preparation and characterisation of C_{119} [1]

Andrei Gromov [a], Stephan Ballenweg [a], Sabine Giesa [b], Sergei Lebedkin [c], William E. Hull [d], Wolfgang Krätschmer [a]

[a] *Max-Planck-Institut für Kernphysik, Postfach 103980, D-69029 Heidelberg, Germany*
[b] *Organisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany*
[c] *Forschungszentrum Karlsruhe, Institut für Nukleare Festkörperphysik, Postfach 3640, D-76021 Karlsruhe, Germany*
[d] *Deutsches Krebsforschungszentrum, Zentrale Spektroskopie, Im Neuenheimer Feld 280, D-69120 Heidelberg, Germany*

Received 17 December 1996; in final form 30 January 1997

Abstract

Thermolysis of $C_{120}O$ at 550–600°C yielded a soluble product fraction containing C_{60}, C_{119} and higher-mass species. Using a two-step HPLC procedure two species, both with molecular weight corresponding to C_{119}, were isolated in 3.5% and 2% yield. The 125.76 MHz ^{13}C-NMR spectrum of the latter more stable product obtained from ^{13}C enriched samples proved that this species consists of two C_{58} cages bridged by three sp^3 carbons, two of which are equivalent. NMR-consistent C_{119} structures have been investigated by molecular modeling and turned out to exhibit C_2 symmetry.

1. Introduction

The 'classical' fullerenes contain only an even number of quasi-sp^2 carbon atoms in a closed-cage structure in which pentagons are completely surrounded by hexagons [1]. However, McElvany et al. [2] discovered the odd-numbered clusters C_{119}, C_{129} and C_{139} in the thermal-desorption mass spectra of a toluene extract of commercial soot and in the spectra of the products of ozone–fullerene reactions. Further studies showed that C_{119} could be detected in the mass spectra of thermally treated $C_{60}O$ [3] and $C_{120}O$ [4]. The question arose whether these clusters are open-shell 'classical' fullerene species with dangling bonds, or dimeric fullerene derivatives containing both sp^2 and sp^3 carbon atoms. For example, Taylor proposed for C_{119} a dimeric structure with three non-equivalent sp^3 carbons, in which two non-equivalent cages are linked via one common sp^3 carbon in a spirane structure with C_s symmetry [5]. Alternatively, first-principles molecular dynamics [6] and semi-empirical quantum chemical calculations [7] predicted a 'peanut'-shaped structure for the most stable isomer of C_{119}. This structure displays C_2 symmetry with two cages bridged via three sp^3-hybridised carbon atoms, two of which are equivalent.

However, the question remained: Is C_{119} only a transient species produced during the desorption/ionisation process in the mass spectrometer or can it actually be isolated as a stable compound? In this Letter we report on the production and characterisation of bulk amounts of C_{119} as a stable dimeric fullerene compound.

[1] Dedicated to Professor Rolf Gleiter on the occasion of his 60th birthday.

PII S0009-2614(97)00129-2

2. Production and isolation procedure

We have studied the thermolysis of the dimeric [60]fullerene oxide $C_{120}O$ by means of HPLC and matrix-assisted laser desorption/ionisation time-of-flight (MALDI–TOF) MS [8]. $C_{120}O$ was produced according to Ref. [4] and was coarsely separated from excess C_{60} by adding hexane to an *o*-dichlorobenzene (ODCB) solution of the reaction mixture [9]. The precipitate contained up to 80% $C_{120}O$ and was used without further purification. Thermolysis was carried out at 300–600°C. Typically, samples of solid $C_{120}O$ were heated in a single step under argon for 1–3 h and then dissolved in ODCB. The soluble portion was analyzed by HPLC and MALDI–TOF MS. At temperatures of up to 500°C only negligible amounts of C_{119} were produced. After reaction at 550–600°C the soluble portion (65–70 wt.-% relative to the starting material) contained C_{119} (6–7%, HPLC), reconverted C_{60} (ca. 90%, HPLC), and higher-mass species. C_{119} was also produced by direct heating of solid $C_{60}/C_{60}O_n$ mixtures ($n = 1$–4), but with lower yields.

C_{119} was coarsely separated from C_{60} as described above for $C_{120}O$ and further purified using a two-step HPLC process. First, a Cosmosil 5PBB column with ODCB as eluent was used to remove the remaining C_{60} and higher-mass species. The fraction containing mainly C_{119} (up to 85%) was then passed through a Cosmosil Buckyprep column with toluene as eluent. Fig. 1 shows a typical chromatogram for the second separation step. According to the MALDI–TOF MS analysis fraction **1** corresponds to C_{60}, whereas fractions **2** (yield 3.5%) and **3** (2%), which were eluted together during the first separation step, can both be assigned to C_{119} but with different fragmentation patterns (Fig. 2). Fraction **3** exhibited an intense molecular ion peak at m/z 1429.3 and only minor fragmentation to C_{60} (m/z 720.1; Fig. 2a). Fraction **2** also gave a peak at m/z 1429.2, but readily fragmented to C_{60} (m/z 720.7), and species formed from C_{119} by subsequent loss of C_1 (m/z 1417.2), and several C_2 units (m/z 1393.2, 1369.3; Fig. 2b). Peaks at $m/z \approx 736$ and $m/z > 1429$ in both spectra may be the result of oxidation during preparation of the MS samples.

C_{119} is oxygen sensitive and decomposes within hours under ambient conditions. Thus, the HPLC separation was carried out under an inert atmosphere. Under argon C_{119} from fraction **3** is stable in a refrigerator for weeks and was used for NMR studies. In contrast, fraction **2**, whose characterisation is in progress, gradually decomposes under these conditions, with C_{60} being one of the products.

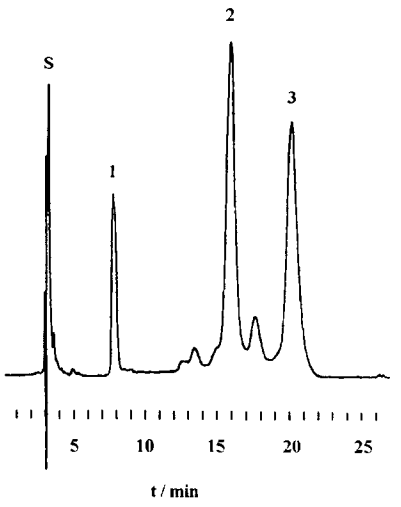

Fig. 1. HPLC chromatogram of the mixture containing C_{119} after the first separation step. S: solvent, *t*: retention time; peaks **1**, **2**, and **3** are assigned in the text. Conditions: Cosmosil Buckyprep column (250 × 4.6 mm), toluene eluent, flow rate 1.0 ml min^{-1} at 60 bar, optical detection at 340 nm.

3. ^{13}C-NMR characterisation

Because of the low solubility of C_{119}, a sample was prepared starting from C_{60} enriched to ca. 7% in ^{13}C [10]. The purified C_{119} sample (ca. 0.5 mg) was dissolved in 0.25 ml ODCB (not deuterated) containing 24 mM $Cr(acac)_3$ as paramagnetic relaxation agent. The sample was placed in a 5-mm NMR tube, and a 2-mm capillary containing acetone-d_6 was inserted to provide a field/frequency deuterium lock.

^{13}C-NMR at 125.76 MHz (11.7 T) was carried out at 30°C with a Bruker AM-500 FT-NMR spectrometer using a standard 5 mm $^1H/^{13}C$ probehead. ^{1}H decoupling was performed using the WALTZ-16 composite-pulse technique [11] (2 W, 90° pulse = 90 μs). The relaxation agent reduced the T_1 relaxation times for the ODCB signals to ca. 0.6–0.9 s.

The three strong solvent resonances in the spectral region for sp^2 carbons (> 1000 times more intense than the C_{119} signals) resulted in artifact signals at a level of ca. 0.1–1%. Therefore, a *J*-modulated spin–echo pulse sequence [12] without sample spinning and with a dephasing period $\tau = 0.5/J$ of 3.05 ms (corresponding to $^1J_{CH} = 164$ Hz) without ^1H decoupling followed by a rephasing period with decoupling was used to suppress the solvent CH carbon signals without effecting the quaternary carbon sig-

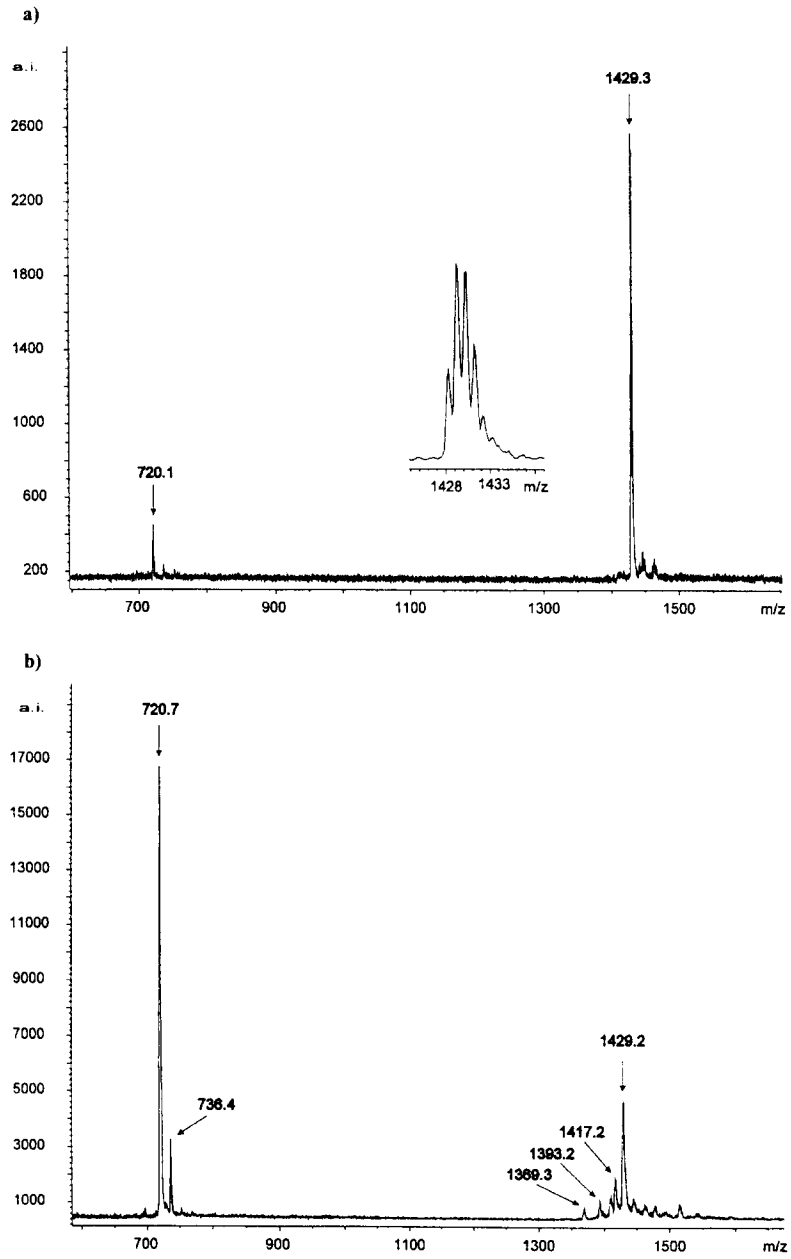

Fig. 2. MALDI–TOF mass spectrum (negative-ion mode, benzo[a]pyrene matrix) of (a) fraction 3 (the expanded region around the molecular ion peak is shown in the inset) and (b) fraction 2 (for assignments see text).

nals from C_{119} or C–Cl in ODCB. This technique avoided the possible intensity distortions which direct irradiation of solvent resonances could have caused and resulted in usable spectra despite some residual decoupling artifacts.

Two separate data acquisitions with different offset frequency and decoupler power were performed; Measurement 1: spectral width = 27777 Hz, time domain = 64k points, repetition time = 3.6 s, 61440 transients in 60 h; Measurement 2: spectral width 26315 Hz with 64k data points, repetition time = 2.25 s, 76800 transients in 48 h. Some of the artifact peaks were shifted or absent in one spectrum relative to the other. Finally, an identically prepared solvent sample without C_{119} was measured with the parameters of Measurement 2. In this way all true C_{119} signals and the artifact signals could be clearly distinguished. Table 1 summarizes the chemical shifts of the resolved resonances observed in Measurement 2 (see Fig. 3) and the signal integration data obtained independently from both measurements. A total of 55 sp^2 carbon resonances, integrating to $2 \times 58 = 116$ carbons could be resolved in the range 151–134 ppm, while 2 sp^3 carbon resonances were found at

Table 1
^{13}C-NMR analysis of C_{119} in *o*-dichlorobenzene at 30°C

Peak	^{13}C shift [a]	Integrals [b]		Peak	^{13}C shift [a]	Integrals [b]	
1	150.841	1.80	2.38	28	143.552		
2	149.685	2.36	2.24	29	143.531		
3	149.387	2.00	1.93	30	143.514	**5.57**	**5.63**
4	148.001	**5.50**	**6.25**	31	143.389	2.28	2.54
5	147.809	1.96	2.01	32	143.301	2.09	
6	147.575	1.94	1.61	33	143.283	2.14	**4.50**
7	147.464	1.73	1.95	34	143.130	2.30	2.26
8	146.900	**3.93**	**4.31**	35	143.067	1.87	2.14
9	146.444	2.19	2.33	36	142.694	2.25	2.63
10	146.353	2.90	2.89	37	142.469	1.87	2.00 [c]
11	146.210	2.00 [c]	1.89	38	142.136	1.99	2.15
12	146.079	1.93	1.70	39	142.077	2.11	2.09
13	146.006	1.93	2.35	40	141.389	2.09	2.41
14	145.987	1.99	2.06	41	141.133	1.76	2.40
15	145.919	1.76	1.81	42	141.051	1.97	1.76
16	145.673	2.03	2.49	43	140.476	2.01	2.01
17	145.651	2.36	2.40	44	140.122	1.76	2.33
18	145.603	1.79	2.10	45	139.819	1.97	2.09
19	145.369	1.71	2.60	46	138.948	1.83	2.17
20	145.305	2.38	2.10	47	138.681	1.16	2.46
21	144.625	1.87	2.09	48	138.243	1.55	2.22
22	144.555	2.08	2.07	49	137.682	1.85	1.67
23	144.459			50	137.023	1.63	2.01
24	144.443	**3.34**	**4.07**	51	135.888	2.65	1.75
25	143.917	2.20	2.33	52	135.709		
26	143.750	1.71	2.42	53	135.700	**3.18**	**3.99**
27	143.707	2.58	1.89	54	135.589	2.30	1.73
				55	134.913	1.97	2.61
56	73.728	**1.86**	**2.40**				
57	57.158	**0.80**	**1.25**				

[a] Chemical shifts in ppm relative to ODCB C–Cl at 132.530 (rel. to TMS = 0).

[b] Relative signal integrals are from Measurements 2 and 1, respectively (see text). The integrals for 46 resolved sp^2 carbon signals have nominal values of 2.0 (±20%). In addition (values in bold face): peak 4 = 6 C, peak 8 = 4 C, peaks 23 + 24 = 4 C, peaks 28 + 29 + 30 = 6 C, peaks 52 + 53 = 4 C, for a total of 116 sp^2 carbons; peak 56 = 2 C and peak 57 = 1 C for a total of 3 sp^3 carbons.

[c] This integral was normalized to 2.00.

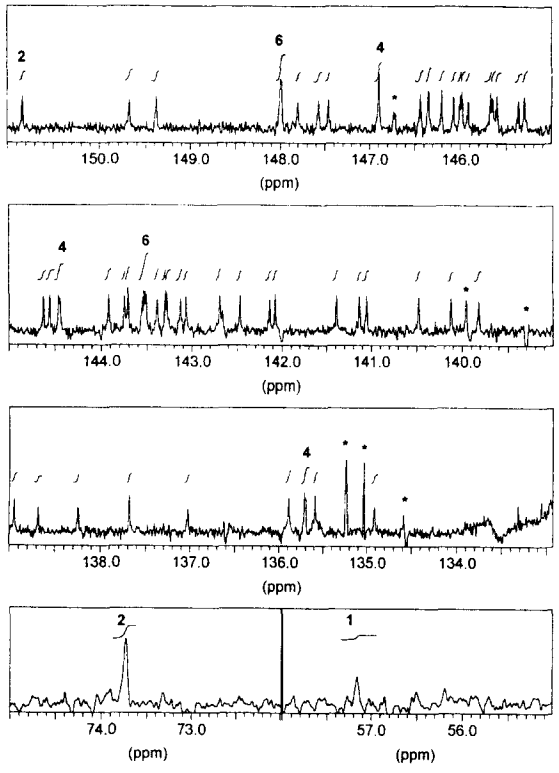

Fig. 3. Expanded traces plotted from the ^{13}C-NMR spectrum of ca. 0.4 mM C_{119} (7% ^{13}C) in *o*-dichlorobenzene containing 24 mM $Cr(acac)_3$ (Measurement 2: 48 h acquisition). Bottom trace: sp^3 carbon signals with integral ratio of 2:1 (3 Hz line broadening applied). Other traces: sp^2 resonances (Lorentz–Gauss resolution enhancement); artifact signals (see text) are marked with *. Integrals for overlapping resonances are accordingly labeled for '4' or '6' carbons (see Table 1).

73.73 and 57.16 ppm, with integrals of 2 and 1, respectively. Based on the integral of the ODCB C–Cl two-carbon signal (concentration ca. 8.87 M), the actual concentration of C_{119} in the sample was estimated to be ca. 2.8 mM for 1.1% ^{13}C or ca. 0.4 mM, assuming 7% enrichment.

4. Molecular modeling

The MS and ^{13}C-NMR data of C_{119} provide convincing evidence for a structure with two-fold symmetry containing two C_{58} cages of sp^2 carbons bridged by three sp^3 carbons with one unique central carbon on a symmetry element. There are various strategies for constructing such C_{119} structures. For example, Adams et al. [6] began with a C_{59} cage with three dangling bonds around a 'hole' (C_{60} with one carbon atom missing). Such a cage was coupled with C_{60} [6], yielding Isomer **I** (Fig. 4) with C_2 symmetry.

We have developed a general approach for C_{119} modeling by beginning with a C_{58} 'basket' structure, obtained by extracting a C_2 unit from C_{60}. Loss of a 6,6-junction results in a C_{58} cage with C_{2v} symmetry and four open valences at hexagonal sp^2 vertices around a 12-atom perimeter (we call this an 'h4' basket); loss of a 5,6-junction gives a cage with C_s symmetry and two pentagonal and two hexagonal vertices around a 13-atom perimeter ('p2h2' basket). Two baskets can be linked by a C_3 chain of sp^3 carbons which contains exactly the required 3 + 2 + 3 = 8 open valences. There are three sterically accessible types of bridges which we define as A = 2.1.1/1.1.2 or the enantiomeric form 1.1.2/2.1.1, B = 1.2.1/2.0.2, and C = 1.0.3/2.2.0 or 3.0.1/0.2.2; in this nomenclature each digit denotes the number of bonds for the 'left.center.right' sp^3 carbons to the 'top/bottom' basket. For example, Isomers **I**, **III** and **IV** in Fig. 4 have a Type A bridge (defined with the central sp^3 carbon oriented towards the viewer), whereas Isomer **II** exhibits a Type B bridge.

There are three possible isomeric structures which can be formed with a 2.1.1/1.1.2 Type A bridge

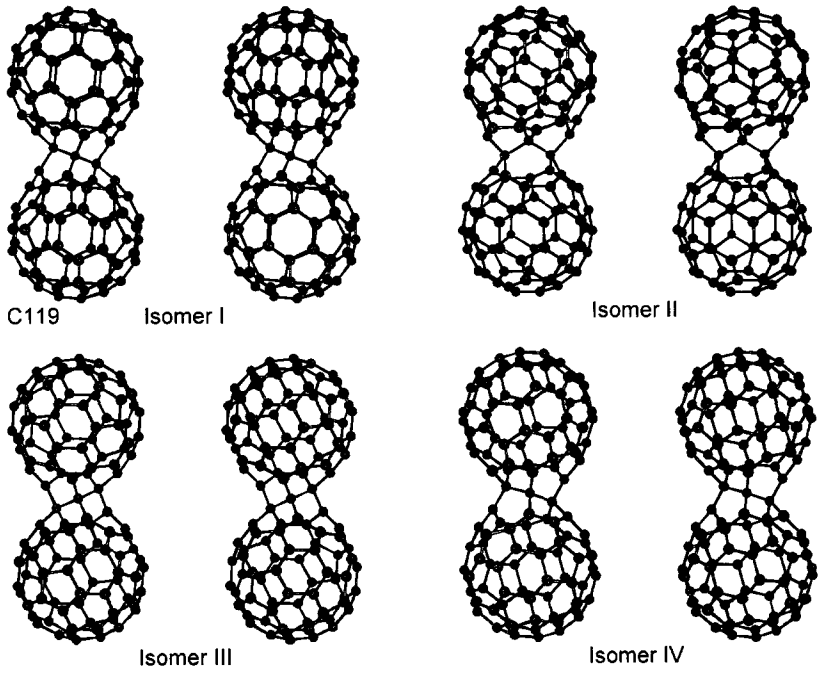

Fig. 4. Stereo views of the four possible C_{119} structural isomers which have the lowest calculated energies and are consistent with the ^{13}C-NMR data. A C_3 unit of sp^3 carbons at the center of each structure connects two C_{58} sp^2 cages. The C_2 symmetry axis is perpendicular to the page for **I**, **III**, **IV** and along the cage axis in **II**. The relative energies (kJ mol^{-1}) calculated with AM1 and MM2, respectively, are: **I** (0, 0), **II** (232, 73); **III** (220, −6); **IV** (220, 34). **I** is the structure proposed by Adams et al. [6].

between two 'h4' baskets. Isomer **I** (Fig. 4), and a second, higher-energy isomer (not shown) both possess C_2 symmetry, with the rotation axis being in the sp^3 plane. The latter isomer features adjacent pentagons and does not satisfy the 'isolated pentagon rule' [1,13]. The third possible isomer has no symmetry. The three isomers differ in the directional properties (e.g. clockwise or counter-clockwise) of the sequence of five- and six-membered rings around the perimeter of each basket. Each of the three isomers has an enantiomeric form containing a 1.1.2/2.1.1 bridge.

If two 'h4' baskets are connected by a Type B bridge, the C_2 axis of the model structure coincides with the vertical basket axes (see Isomer **II** in Fig. 4). A total of four bridging combinations are possible, giving two isomers (each with an enantiomer). A Type C bridge between 'h4' baskets also results in two isomers and their enantiomers, but without symmetry.

Two 'p2h2' baskets can also be combined using the same types of bridges. Two examples of Type A bridges are shown as Isomers **III** and **IV** in Fig. 4, and these also feature a perpendicular C_2 axis. The reduced symmetry of the 'p2h2' basket implies that Type B and C bridges cannot produce symmetrical structures.

Energy calculations performed using a π-SCF-modified MM2 force field method indicated that of all isomers with two-fold symmetry, those in Fig. 4 (see caption) had the lowest energies. These structures were then analyzed further using the semi-empirical AM1 method, and **I** was found to have the lowest heat of formation.

5. Discussion

Considering the starting material for the formation of C_{119}, it appears reasonable to assume a dimer-like structure for this all-carbon species. The ^{13}C-NMR results confirm conclusively that this substance has two-fold symmetry about the unique central atom of a three-carbon sp^3 bridge. Moreover, these data indicate the presence of a single isomer which may be in two enantiomeric and NMR-indistinguishable forms. Each of the modeled isomers in Fig. 4 is consistent with the NMR results, but the spectra of these isomers should be distinguishable. MM2 calculations give similar energies for **I** and **III** but significantly higher energies for **II** and **IV**, while AM1 clearly favors **I**.

At the moment we cannot offer a detailed, experimentally proven mechanism for the formation of C_{119} during the pyrolysis of $C_{120}O$. Experiments measuring the gas released from heated $C_{120}O$ by means of IR spectroscopy [8] or MS have shown a significant development of CO and CO_2 at temperatures above 450°C. The release of CO suggests that $C_{120}O$ may be the precursor of C_{119}.

The structure of $C_{120}O$ consists of two [60]fullerene cages connected via 6,6-junctions in a furan-like bridge [4,14]. As a working hypothesis we note that in a formal sense CO can be released from the bridging 6,6-junctions by the breakage of four single bonds, leading to the formation of 'h4' rather than 'p2h2' baskets. The resulting open valences can be closed with two single bonds to give a Type C bridge between 'h4' baskets, for example. The resulting asymmetric structure has a calculated energy which is higher than that for any of the isomers of Fig. 4, and this structure can readily rearrange via two opposing 1,2-shifts of σ-bonds to give **I** or **II**, for example. In any event, a relatively simple sequence of individual bond-breaking and bond-formation steps (electron migrations) can lead to a Type C intermediate or to Type A products directly; however, the details of such a process are still a matter of conjecture and exceed the scope of this report. Structures such as **III** or **IV**, involving 'p2h2' baskets, are not directly accessible by a simple mechanism. Therefore, from energetic and reasonable mechanistic standpoints, we consider the dimeric fullerene derivative **I** to be the most likely structure for the stable C_{119} isomer.

Acknowledgements

AG, SB, and WK wish to thank the Deutsche Forschungsgemeinschaft and SL is grateful to the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie for financial support. We are thankful for the assistance of Dr. J. Gross in acquiring mass spectra, Dr. P. Bischof in carrying out the AM1 calculations and Mrs. M. Schickedanz

in performing the HPLC separation. We further thank Dr. G.B. Adams for providing unpublished data.

References

[1] H.W. Kroto, Nature 329 (1987) 529.
[2] R.S.W. McElvany, J.H. Callagan, M.M. Ross, L.D. Lamb and D.R. Huffman, Science 260 (1993) 1632.
[3] R.D. Beck, G. Bräuchle, C. Stoermer and M. Kappes, J. Chem. Phys. 102 (1995) 540.
[4] S. Lebedkin, S. Ballenweg, J. Gross, R. Taylor and W. Krätschmer, Tetrahedron Lett. 36 (1995) 4971.
[5] R. Taylor, J. Chem. Soc. Chem. Commun. (1994) 1629.
[6] G.B. Adams, J.B. Page, M. O'Keeffe and O.F. Sankey, Chem. Phys. Lett. 228 (1994) 485.
[7] E. Albertazzi and F. Zerbetto, J. Am. Chem. Soc. 118 (1996) 2734.
[8] A. Gromov, S. Lebedkin, S. Ballenweg and W. Krätschmer, in: Fullerenes and fullerene nanostructures, proceedings of the international winterschool on electronic properties of novel materials, eds. H. Kuzmany, J. Fink, M. Mehring and S. Roth (World Scientific, Singapore, 1996) p. 460.
[9] S. Lebedkin and A. Gromov, unpublished results.
[10] A. Gromov, S. Lebedkin, S. Ballenweg, A.G. Avent, R. Taylor and W. Krätschmer, J. Chem. Soc. Chem. Commun. in press.
[11] A.J. Shaka, J. Keeler and R. Freeman, J. Magn. Reson. 53 (1983) 313.
[12] C. LeCocq and J.Y. Lallemand, J. Chem. Soc. Chem. Commun. (1981) 150.
[13] S.J. Austin, P.W. Fowler, D.E. Manolopoulos, G. Orlandi and F. Zerbetto, J. Phys. Chem. 99 (1995), 8076.
[14] A.R. Smith, H. Tokuyama, M. Strongin, G.T. Furst and W.J. Romanov, J. Am. Chem. Soc. 117 (1995) 9359.